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(54) Process and composition for extrusion of Ziegler-Natta catalyzed olefin polymers.

(57) A non-volatile, acid acceptor which is soluble in polyolefins is added to a film grade polyolefin resin composition to prevent gel streaking/pinstriping or corrosion during film extrusion processes. The acid acceptor has a molecular weight greater than 180 with less than 5% by weight volatiles at 180°C as measured by a thermal evolution analysis.

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PROCESS AND COMPOSITION FOR EXTRUSION OF ZIEGLER-NATTA CATALYZED OLEFIN POLYMERS

This invention relates to anti-gel compounds useful for reducing optical degradation phenomena in extruded polyolefin film. The compounds also are useful for preventing corrosion during high temperature processing of polyolefin film.

Polyolefin resins such as polyethylene have been used for a number of years for the preparation of films by extrusion processes. Unlike high pressure, free radical polymerized polyethylenes, low pressure, low density polyethylenes prepared in the presence of Ziegler-Natta catalysts commonly develop gel-like defects when extruded, e.g., when extruded as blown films. In a blown film process, polyethylene pellets or granules are melted and extruded from an annular die to form a film envelope. In the extruder and die system, there are typically "dead spots" or "hangup areas" where molten polyethylene does not move rapidly, resulting in long heat histories for portions of the melt. As portions of the polymer are flushed from these hangup areas, they cause optical degradation phenomena in the film, known as "pinstriping" and "gel streaking".

By "pinstriping" is meant haze bands resulting from accumulations of micro-gels which are aligned in the machine direction during the film forming process. By "gel-streaking" is meant surface roughness in the form of the inclusion, either singularly or in rows, of "v-shaped" gels ("arrowheads" or "chevrons"), streaks of soft gels, or, in extreme cases, film texture completely permeated by soft gels. Such optical degradation phenomena not only detract from film optical and

mechanical strength properties, but also can cause severe problems with respect to maintaining bubble geometry during the film forming process.

Because of the fact that the extrusion processes usually involve the use of relatively high extrusion temperatures and prolonged extrusion times, in commercial practice, various anti-oxidants, such as hindered phenolics, are admixed with the polyolefin resin, to prevent undesirable degradation of the polymer during the preparation of the film. When such anti-oxidants are used, however, with the film forming grades of polyolefins in certain types of extrusion equipment, the anti-oxidants appear to pronounce, if not create, gel-streaking and pinstriping in the products thus formed.

Many solutions have been proposed to eliminate gel-streaking and pinstriping. For example, it is known to physically remove the catalyst residue, prior to extrusion, by leaching the reaction product of polymer and catalyst with alcohols, aqueous acid, water, or treating the polymer and catalyst with propylene oxide followed by an alcohol or water wash and the like. Such treatments usually produce white polymers initially, but a yellow or tan color returns when the polymers are subjected to molding and/or heating operations. In order to avoid this undesirable color formation, it is usually necessary to use a second or even a third clean-up procedure requiring the use of large quantities of deactivating materials. Another practice in the art involves drying the after-treated polymer prior to fabrication. Because they usually must be repeated several times in order to obtain a polymer having acceptable color upon exposure to heat, such clean-up procedures are both expensive and time consuming. Illustrative of such prior art treatments

are those disclosed in U.S. patents 3,925,341; 3,962,199; 3,247,351; 4,029,877; 4,117,219; 3,299,027; 3,923,760; 3,308,105; and 4,098,990.

Other treatments disclosed in the prior art involve the addition of compounds to the polymer prior to fabrication in order to complex with the harmful components in the catalyst residue and deactivate them. Illustrative of these prior art treatments are those disclosed in Canadian patent 961,998, U.S. patent 4,013,622 and in U.S. patent 3,773,743.

For example, U.S. patent 3,773,743 discloses a method for improving the stability and color of olefin polymers by deactivating their Ziegler-Natta catalyst residues. This method involves high temperature (190°C-250°C) processing with hydroxyl compounds (H_2O and primary alcohols) and with an organic base such as an alkyl amine; aryl amine; Li, Ca and Zn salts of carboxylic acids; trialkyl phosphites; and metal alkoxides. The concentration disclosed for the hydroxy source is the range of 0.5 to 1.5 weight percent and a concentration of 50 to 2500 parts per million (ppm) is disclosed for the organic base. At the processing temperatures disclosed, some of the organic bases and the hydroxy sources would be volatile and cause foaming of the product if the processing were not done in a way to remove volatiles, e.g., as in devolatilizing esters.

In high temperature processing of Ziegler-Natta catalyzed polyolefin resins, such as in slot cast or blown film extrusion, it has been observed that the chloride catalyst residue present in the resins may cause corrosion of the processing equipment. For example, corrosion pitting has been observed on both the chill roll and internal adaptor and die surfaces during slot cast film extrusion. Internal adaptor and die surfaces of blown

film extrusion equipment also are subject to corrosion. Deactivation of the catalyst residue has been required in a costly separate step prior to high temperature ($\geq$210°C) processing of the resin.

An object of the present invention is to provide a film forming extrudable composition comprising a Ziegler-Natta catalyzed polyolefin and an extruded film made from such extrudable composition, which film is free from gel streaking.

Another object of the present invention is to provide a process wherein Ziegler-Natta catalyzed polyolefin film forming compositions may be extruded without optical degradation phenomenon appearing within the extruded film.

Another object of the present invention is to provide an anti-gel compound, which when added to Ziegler-Natta catalyzed polyolefins is useful in removing or reacting with the chloride residue in said polyolefins to prevent gel streaking or pinstriping from occurring in subsequent extrusion processes.

An object of the present invention is to provide an improved process for extruding tubular blown polyolefin film substantially free of Ziegler-Natta chloride residues.

Another object of the present invention is to provide an improved process for producing, at high temperatures ($\geq$210°C), an extruded film, sheet or molded articles made from Ziegler-Natta catalyzed polyolefin resin, which process is substantially free from corrosion.

This invention is based on the discovery that an optical degradation phenomenon, known as gel streaking and pinstriping, present in extruded Ziegler-Natta catalyzed

polyolefins, can be substantially prevented through the addition of small amounts of an organic compound of high molecular weight and relatively low volatility. The organic compound comprises a hydrogen chloride acceptor having a molecular weight greater than 180 with less than 5% by weight volatiles at 180°C as measured by thermal evolution analysis (TEA). According to the present invention, the incidence of gel streaking or pinstriping in the film during the extrusion of low pressure, low density ethylene hydrocarbon polymer resin is minimized through the use of a composition comprising:

a majority of a low pressure, low density ethylene hydrocarbon polymer resin; and

a minor amount of an anti-oxidant and a hydrogen chloride acceptor as defined herein. This invention also relates to an improved method of extruding low pressure, low density ethylene hydrocarbon polymer resins which comprise incorporating minor amounts of an anti-oxidant and a hydrogen chloride acceptor into said resin prior to extrusion thereof.

In one aspect, the present invention relates to an extrudable film forming composition which, when extruded, forms a film essentially devoid of gel streaking and pinstriping, the film forming extrudable composition comprising a polyolefin resin, an anti-oxidant and anti-gel compound. The polyolefin resin contains chloride residue from a Ziegler-Natta catalyst used in its preparation. The anti-oxidant is present in an amount sufficient to prevent oxidation of the film during extrusion processing and subsequent storage thereof. The anti-gel compound is present in an amount sufficient to neutralize the chloride residue in the polyolefin, which amount

also should be at least about 0.8 times the amount of anti-oxidant present. Preferably, the amount of anti-gel compound is at least equal to the amount of anti-oxidant present.

The amount of anti-gel compound necessary to neutralize the chloride residue should be greater than about 5 times, preferably greater than about 10 times, and most preferably greater than about 20 times the amount of chloride residue present. When the ratio becomes too high, particularly at the higher chloride levels, e.g., at 200 ppm chloride residue, the anti-gel compound can exude to the polymer air interface and adversely affect polyolefin surface properties such as sealing, treatability and coefficient of friction. Below a 5 to 1 ratio, the amount of anti-gel compound may not be sufficient to neutralize the chloride residue to retard gel streaking etc.

Chloride residue from a Ziegler-Natta catalyst is typically present in a concentration between about 5 and about 500 ppm based upon the polyolefin. Chloride residue concentrations between about 5 and about 50 ppm are typical for polyethylene and chloride residue concentrations between about 10 and about 500 ppm are typical for polypropylene and polybutene made with Ziegler-Natta catalysts.

Anti-oxidants in a concentration of 20 to 500 ppm are typically added to polyethylene resin compositions. And concentrations of 200 to 5000 ppm of anti-oxidant are typically added to polypropylene or polybutene resin compositions.

In another aspect, the present invention relates to a process for extruding a film forming polyolefin resin based composition into film. The resin based composition comprises a Ziegler-Natta catalyzed film grade polyolefin resin which contains a chloride residue in the range of between about 5 and

about 500 ppm and anti-oxidant in the range of between about 20 and about 5000 ppm based upon the polyolefin resin. The resin based composition is susceptible to gel streaking during formation of the film. This invention is based upon the discovery that such a process may be improved by extruding the resin based composition into the film in the presence of an acid acceptor. The acid acceptor is typically present in a concentration between about 25 and 10,000 ppm, based upon the weight of the polyolefin resin and has a molecular weight $\geq$180 with $\leq$5% by weight volatiles at 180°C as measured by TEA.

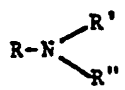
In still another aspect, this invention relates to the discovery that high temperature (above 2 0°C) processing of Ziegler-Natta catalyzed polyolefin resin (containing a chloride catalyst residue) into film can be accomplished without corrosion of the processing equipment by incorporating an acid acceptor as defined herein into the polyolefin resin composition to be processed. The concentration of acid acceptor required to prevent corrosion is between about 25 and 10,000 ppm, based upon the polyolefin resin.

The acid acceptor is uniformly dispersed in the polyolefin based extrusion composition. The dispersion can be effected by various dispersion techniques commonly employed by those skilled in the art of preparing extrudable composition. The acid acceptor could be introduced into the polyolefin either by directly dry blending with a granular polyolefin (e.g., polyethylene) via a V-type blender or by mixing via a Henschel type intensive mixer. The acid acceptor also could be hot compounded into the polyolefin to make a master batch for final letdown using conventional hot processing equipment such as a Banbury mixer, a Werner Pfleiderer twin

screw mixing extruder or a single screw mixer extruder that has pelletization equipment on the head of the extruder.

The Acid Acceptor

The acid acceptor comprises a fatty acid amine of the formula:



wherein R is C_{12-24} alkyl or alkylene;

R' is hydrogen, lower alkyl, an alkanol, 1,3-propylene/diamine or an ethoxy group of the formula $(C-C-O)_xH$, wherein x is an integer between 2 and 5; and

R" is R or R'.

The fatty acid amine used in this invention is normally either liquid or solid at room temperature, has a molecular weight above about 180, and has less than about 5% by weight volatiles at 180°C as measured by TEA. Below molecular weights of 180, volatility becomes a problem, resulting in bloom on the surface of the film or causes plate-out or smoking on high temperature extrusion. This can adversely affect such properties as sealing, treatability and surface characteristics, in general. Increased volatility also can be manifested in foaming of the film extrudate and lensing in the blown film bubble. Too high a molecular weight simply requires more anti-gel compounds. Surface properties also can be affected.

Suitable fatty acid amines according to the present invention include a saturated fatty acid amine such as lauryl amine, mystearyl amine, palmityl amine, stearyl amine, arachidyl amine, behenyl amine and the like; a monounsaturated fatty acid such as oleyl amine and erucyl amine; a di-saturated fatty acid amine such as di-lauryl amine, di-mystearyl amine, dipalmityl

amine, di-stearyl amine, di-arachidyl amine, di-behenyl amine; a di-monounsaturated fatty acid amine such as di-oleyl amine and di-erucyl amine; a mixed saturated and mono-unsaturated fatty acid amine such as lauryl-oleyl amine, lauryl-stearyl amine, oleyl-erucyl amine and the like; lauryl, mystearyl, palmityl stearyl, arachidyl, behenyl, oleyl or erucyl--methanol, ethanol propanol or butanol amines; dimethanol, diethanol, dipropanol or dibutanol--lauryl, mystearyl, palmityl, stearyl, arachidyl, behenyl, oleyl or erucyl amines; dimethyl, diethyl, dipropyl or dibutyl--lauryl, mystearyl, palmityl, stearyl, arachidyl, behenyl, oleyl or erucyl amines; alkoxylated lauryl, mystearyl, palmityl, stearyl, arachidyl, behenyl, oleyl or erucyl amines derived using 2 to 10 mols of ethylene oxide, propylene oxide or butylene oxide; and N-lauryl, mystearyl, palmityl, stearyl, arachidyl, behenyl, oleyl, or erucyl--1,3-propylene diamine.

Olefin Polymers

The extrudable olefin polymers employed in the extrudable compositions of the present invention are normally solid materials, that is, solid at room temperature. Any extrusion grade olefin polymer can be used in the compositions of the present invention. The term "olefin polymer" thus includes homopolymers of the olefins, as well as interpolymers of one or more olefins with each other, and/or up to about 30 weight percent of one or more monomers which are copolymerizable with such olefins. The olefins such as ethylene, propylene, 1-butene, isobutylene, 4-methyl-pentene-1, hexene-1, octene-1, nonene-1, decene-1, as well as interpolymers of one or more of such olefins and one or more other monomers which are interpolymerizable with such olefins, such as other vinyl and diene compounds, i.e., those having the group $-\overset{|}{C}=\overset{|}{C}-$.

Preferred copolymers are the ethylene copolymers such as ethylene/propylene copolymers, ethylene/butene-1 copolymers, ethylene/hexene-1 copolymers, octene-1 copolymers, and the like. Preferred ethylene interpolymers would include two or more of the following: propylene, butene-1, hexene-1, 4-methyl-pentene-1 and octene-1. Preferred propylene interpolymers would include ethylene, butene-1, hexene-1, 4 methyl-pentene-1 and octene-1 as monomers.

Also included in the term polymer are blends of one polymer with one or more other polymers. Illustrative of such blends are ethylene/olefinic polymers with one or more of the following: polypropylene, high pressure low-density polyethylene high density polyethylene, polybutene-1, and polar monomer containing olefin copolymers such as ethylene/acrylic acid copolymers, ethylene/methyl acrylate copolymer, ethylene/ethylacrylate copolymer, ethylene/vinyl acetate copolymer, ethylene/acrylic acid/ethyl acrylate terpolymer, ethylene/acrylic acid/vinyl acetate teropolymer, and the like.

Also included within the term polar monomer containing olefin copolymers are the metallic salts of those olefin copolymers, or blends thereof, which contain free carboxylic acid groups. Illustrative of such polymers are ethylene/acrylic acid copolymer, ethylene/methacrylic acid, oxidized polyolefins, propylene/acrylic acid copolymer, butene/acrylic acid copolymer and the like.

Illustrative of the metals which can be used to provide the salts of said carboxylic acid polymers are the one, two and three valence metals, such as sodium, lithium, potassium, calcium, magnesium, aluminum, barium, zinc, zirconium, beryllium, iron, nickel, cobalt, and the like.

The preferred olefin polymers for use in the present invention are polymers of ethylene, and the most preferred polymers are those having a melt index of about 0.1 to 10 grams per 10 minutes, a density of about 0.910 to 0.955. Low density ethylene polymer has a density of between approximately 0.910 and 0.925, medium density ethylene polymer has a density of between approximately 0.925 and 0.940, and high density ethylene polymer has a density of between approximately 0.940 and 0.970. Thus, the low density ethylene copolymers are the most preferred olefin polymers to be used in the present invention, although the medium and high density polymers may also be used.

Preferred low pressure, low density ethylene copolymers for use in the present invention include those which may be produced in accordance with the procedures set forth in U.S. Patent Application Serial No. 892,325, filed March 31, 1978, and refiled as Serial No. 014,414 on February 27, 1979, in the names of F.J. Karol et al. and entitled "Preparation of Ethylene Copolymers in Fluid Bed Reactor", and the procedures set forth in U.S. Patent Application Serial No. 892,322, filed March 31, 1978, and refiled as Serial No. 012,720 on February 16, 1979, in the names of G.L. Goeke et al. and entitled "Impregnated Polymerization Catalyst, Process for Preparing, and Use for Ethylene Copolymerization" as well as procedures which will produce ethylene hydrocarbon copolymers with properties as heretofore described. U.S. Application Serial No. 014,414 corresponds to European Patent Application No. 79100953.3 which was opened to the public on October 17, 1979 as Publication No. 4645 and U.S. Application Serial No. 012,720 corresponds to European Patent Application No. 79100958.2 which

was opened to the public on October 17, 1979 as Publication No. 4647. The disclosures of Publications Nos. 4645 and 4647 are incorporated herein by reference.

Other low pressure, low density ethylene hydrocarbon copolymers preferred for use in the present invention are those which may be prepared as described in U.S. Patent 4,011,382, entitled "Preparation of Low and Medium Density Ethylene Polymer in Fluid Bed Reactor" by I.J. Levine et al., the disclosure of which is incorporated herein by reference.

The olefin polymers may be used in the form of powders, pellets, granules, or any other form that can be fed to an extruder.

The Anti-Oxidants

As noted above, the extrudable compositions of the present invention contain at least one anti-oxidant for the olefin polymer. These anti-oxidants are present in stabilizingly effective quantities. Such amounts are about 0.002 to 0.5, and preferably about 0.01 to 0.05, percent by weight, based on the weight of the olefin polymer. The anti-oxidant stabilizers which may be employed in the compositions of the present invention include all those polyolefin anti-oxidants commonly employed in olefin polymer based film extrusion compositions. These materials are such as are capable or providing anti-oxidant protection at processing temperatures of the order of about 275 to 650°F, or higher.

Such anti-oxidant stabilizers include hindered phenols, such as p-hydroxyphenylcyclohexane; di-p-hydroxyphenylcyclohexane dicresylolpropane; tertiary butyl para cresol; 2,6-di-tert-butyl-p-cresol; 2,4,6-tri-tert-butylphenol; octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate; tetra bis[methylene 3-

(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane; 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene; tris(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanate; 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6 dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione; and bis-[3,3-bis-4'-hydroxy-3'-tert-butyl-phenyl)-butanoic acid]-glycol ester, condensation products of dialkylphenols with formaldehyde, reaction products of phenol with styrene, 1,1'-methylene-bis(4-hydroxy-3,5-tert-butyl-phenol), 2,2'-methylene-bis-(4-methyl-6-tert-butylphenol), 2,6-(2-tert-butyl-4-methyl-6-methylphenol)-p-cresol, phenylethyl-pyrocatechol, phenolisopropylpyrocatechol, 1,1,3-tris(2'-methyl-5'-t-butyl-4-hydroxy phenol)butane, 2,2-methylene-bis[6-(α-methylcyclohexyl)-4-methylphenol], 1,3,5-trimethyl-2,4,6-tris-(3',5'-di-t-butyl-4-hydroxybenzyl)benzene and α-naphthol; and sulfur containing compounds such as 2,2'-thio-bis-(4-methyl-6-tert-butylphenol), 4-4'-thio-bis-(3-methyl-6-tert-butylphenyl), distearyl thio di propionate and dilauryl thiodipropionate; and phosphite compounds such as tri(mixed mono and dinonyl phenyl)phosphites; phosphite esters of lauryl and stearyl alcohol; di-stearyl-pentaerythritol-diphosphite; bis(2,4-di-tert-butyl-phenyl)pentaerythritol diphosphite; and tri-2,4-di-tert-butyl-phenyl phosphite ester.

The preferred primary or hindered phenolic antioxidant stabilizers which are employed in the compositions of the present invention are 2,6-ditertiary butyl paracresol, or butylated hydroxy toluene (BHT); octadecyl-3-(3,5-di-tert-butyl-4-hydroxy phenyl)propionate (Irganox 1076); or tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane. The preferred secondary stabilizers include dilauryl thiodipropionate (DLTDP); distearyl thiodipropionate (DSTDP); tri(mixed mono and

dinonyl phenyl) phosphite (Polygard); di-stearyl-pentaerythritol-diphosphite (Weston 618).

The hindered phenolic anti-oxidants may be used individually or in various combinations with one another or the secondary stabilizers in the compositions of the present invention. Other additives include slip agents such as fatty acid amides, inorganic antiblocks such as finely divided silica or calcium carbonate, cling agents, fillers or colorants.

Extrudable Compositions

The extrudable compositions of the present invention may be used in any of the forms of such compositions which are commonly employed in the extruded film arts, such as compounds modified with various slip and anti-block additives for specific end use applications.

These extrudable compositions are thermoplastic in nature. In addition to the olefin polymer, anti-gel compounds, anti-oxidant, the compositions of the present invention may contain other adjuvant materials which are commonly employed in olefin polymer-based extrudable film compositions. Such other adjuvants would include plasticizers, fillers, pigments, lubricants, slip agents, modifiers and similar materials.

The fillers which may be used in the olefin polymer-based extrudable compositions of the present invention are the fillers which are commonly used with such polymers. The fillers are used in amounts which correspond to about 1 to 20 percent by weight, based on the weight of the olefin polymer. Such fillers would include materials such as carbon black, titanium dioxide, clays, diatomaceous earth, calcium silicates and others known in the art.

The plasticizers which may be employed in the olefin polymer-based extrudable compositions of the present invention are the plasticizers which are commonly used with such polymers. The plasticizers are used in amounts which would correspond to about 1 to 25 percent by weight based on the weight of olefin polymer. Such plasticizers would include materials such as phthalates, phosphates, adipates, azelates, amine based polyols, and a number of other similar products.

The lubricants which are commonly employed in the olefin polymer-based extrudable compositions are the lubricants which are commonly used with such polymers. The lubricants are used in amounts which correspond to about 0.02 to 0.2 percent by weight of lubricant agent based on the weight of the olefin polymer. Examples of such lubricants are fatty acid amides such as stearamide, oleamide, behenamide and erucamide.

Extruding Conditions

The extrudable conditions of the present invention are particularly designed for use in equipment utilized for tubular film, cast film and extrusion coating products. Such equipment may have hold-up areas or areas of stagnation that retard the flow of extrudate therethrough, leads to the development of gel streaking and pinstriping in the absence of the use of the anti-gel additives of the present invention. In such equipment the polyolefin based extrudable compositions are subjected to extrusion temperatures of about 275 to 650°F, and preferably about 375 to 650°F, under varying conditions of head pressure, and for periods of time of about 0.5 to 10 minutes.

The film is usually prepared in sheets which are about 0.1 to 10 mils thick.

According to the present invention, the polyolefin

resin compositions are not exposed to post-reactor high temperature compounding or finishing which could introduce hydroperoxides into the composition prior to film extrusion. Instead the acid acceptor is added via a master batch or by directly dry blending it into the granular polyolefin resin prior to extrusion thereof. Another advantage of this invention is that gas treatment (e.g., with propylene oxide) after polymerization of the resin is not required nor are subsequent alcohol washes to remove the propylene oxide or ethylene oxide gas nor the subsequent drying process to remove the alcohol. Also unnecessary are the need for devolatilization of alcohols of water which could be added to neutralize and break down catalyst residue.

Another advantage of the present invention is that the fatty acid amines may be incorporated into the polyolefin based resin composition without adversely affecting other additives normally used in such compositions such as hindered phenolic anti-oxidants and phosphites, slip/anti-block materials such as fatty amides, silica or calcium carbonate. The fatty acid amines do not adversely interact with these other additives nor do they cause such problems as discoloration and odor.

Still another advantage of the present invention relates to high temperature extrusion of Ziegler-Natta catalyzed polyolefin resin, i.e., at temperatures above about 210°C up to 300°C. The (Ziegler-Natta) catalyst residue, primarily chlorides present in such polyolefin resins, is liberated as hydrogen chloride during such high temperature processing. The liberated hydrogen chloride can cause removal of chrome plating or corrosion of equipment, both in the adaptor and die sections, as well as on the chill rolls used in high temperature slot cast film extrusion. The hydrogen chloride also will adversely affect

the metal and chrome plated surfaces in blow molding and injection molding equipment. The fatty acid amines of this invention neutralize the catalyst residues and consequently prevent adverse corrosion effects in processing equipment or on a chill roll. The solubility of the fatty acid amines in the polyolefins enables them to reach the catalyst sites to break down and neutralize the chloride residue.

The following examples are illustrative of the present invention and are not intended as a limitation of the scope thereof.

Example 1

Preparation of Polymer Resins

Two low pressure, low density ethylene-butene-1 copolymer resins were prepared according to the procedure disclosed in South African Patent Publication No. 79-01365, published September 22, 1980, entitled "Process for Making Film From Low Density Ethylene Hydrocarbon Copolymer" by W.A. Fraser et al. The properties of the ethylene-1 butene-1 copolymer resins were determined by the following methods:

Density was determined according to ASTM D-1505. A plaque was conditioned for one hour at 100°C to approach equilibrium crystallinity. Density is reported as gms/cm^3.

Melt Index (MI) was determined according to ASTM D-1238, Condition E. It was measured at 190°C and 44 psi and reported as grams/10 minutes.

Flow Index (HLMI) was measured according to ASTM D-1238, Condition F. It was measured at 10 times the weight used in the melt index test above and reported as grams per 10 minutes.

Melt Flow Ratio (MFR) was calculated as Flow Index/

Melt Index.

Ti, Al and Si catalyst residues in the ethylene-butene-1 copolymer in ppm was measured by induction coupled plasma emission spectroscopy.

Cl catalyst residue in the ethylene-butene-1 copolymer in ppm was measured by a Dohrmann micro-coulometric titration system.

One of the ethylene-butene-1 copolymer resins, designated A, had the following properties: a melt index of 1.0; a MFR of 28; a density of 0.918 gm/cm^3; and a catalyst residue in ppm of Ti-2, Al-73, Si-56 and Cl-13.

The other ethylene-butene-1 copolymer resin, designated B, had the following properties: a melt index of 2.0; a MFR of 28; a density of 0.918 gm/cm^3; and a catalyst residue in ppm of Ti-3, Al-89, Si-97 and Cl-16.

Either resin A or resin B was used in the resin compositions of all the subsequent examples herein.

Preparation of Polymer Resin Compositions

One of two methods to prepare polymer resin compositions was employed in the examples. In one method, the components were dry blended in a roll drum for 20 minutes at room temperature with a virgin resin. In the other method, the components were compounded into a masterbatch concentrate utilizing a Banbury batch mixer coupled to a Farrel Birmingham single screw extruder melt pump. The components were mixed in the Banbury mixer for 4 to 5 minutes, dropped at 260°F, and extruded through an extruder melt pump using a throat temperature of 220°F, a barrel temperature of 300°F, and a die temperature of 300°F.

Example 2

A series of experiments were run to demonstrate the effectiveness of the use of a fatty acid amine in polyolefin based film extrusion compositions in order to prevent the formation of gel streaks/pinstriping in the extruded film. Table I below summarizes the results for a number of control formulations which did not contain the fatty acid amine anti-gel compound of this invention. The control formulations were prepared by one of the methods described hereinabove. After the formulations were prepared, films were extruded in a tubular extrusion device for various periods of time to assess gel formation. The film was extruded at 3 lbs/hr with a 385°F melt temperature using a 1-inch Killion 24 to 1 length to diameter extruder equipped with a 1 1/4-inch die with a 0.30 inch gap. No nitrogen purge was used on the extrusion hopper.

The extruded films were approximately 1.5 mils thick. During extrusion, the films were examined periodically for gel streak formation and pinstriping. Table I hereinbelow sets forth the resin compositions that were employed and the results that were obtained with respect to gel streak formation/pinstriping. The number symbols used to designate the visual appearance of the film with respect to gel streaking/pinstriping have the following meanings:

0 - clear of gel streaking/pinstriping

1 - slight gel streaking/pinstriping

2 - moderate gel streaking/pinstriping

3 - severe gel streaking/pinstriping

A review of the information disclosed in Table I shows that the control formulations for runs 2-11 exhibited gel streaking/pinstriping in the extruded films in the presence of hindered phenolic anti-oxidants.

TABLE I

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
1	Resin A	--	1	0
2	Resin A Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] methane	200	2	2
3	Resin A Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate	200	2	2
4	Resin A Di-tert-butyl-para-cresol	200	2	2
5	Resin A 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6 dimethyl benzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione	200	3	3
6	Resin A 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene	200	3	3
7	Resin A Tris(3,5-di-tert-butyl-4-hydroxy benzyl)isocyanate	200	3	3
8	Resin A Bis-[3,3-bis-4'-hydroxy-3'-tert-butyl-phenyl)-butanoic acid]-glycol ester	200	3	3

TABLE I (continued)

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
9	Resin A			
	Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate] methane;	200	3	3
	Di-stearyl-pentaerythritol-diphosphite	200		
10	Resin A			
	Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane;	200	3	3
	Tri-nonyl-phenyl phosphite ester	400		
11	Resin A			
	Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane;	200	3	3
	Di-stearyl-pentaerythritol-diphosphite;	200		
	glycerol monostearate	500		

In another series of experiments, fatty acid amines were added to the control formulations to prevent the formation of gel streaks in the extruded film. The formulations were prepared according to the second method previously described herein. The resin based composition was extruded at 23 lbs/hr with a 410°F melt temperature using a 1 1/2-inch diameter Sterling extruder equipped with a 3-inch diameter spiral die (60 mil gap). No nitrogen purge was used on the extruder hopper. The extruded films were approximately 1.5 mils thick. During extrusion, the films were examined periodically for gel streaking/pinstriping. Table II below discloses control compositions and example compositions for runs 12-20 that were employed and the results obtained with respect to gel streak formation/pinstriping. The number symbols used have the same meaning previously given herein.

A review of the information disclosed in Table II shows that the addition of a fatty acid amine to the control formulations completely, or at least substantially, prevents the formation of gel streaking/pinstriping in the extruded films, even in the presence of hindered phenolic anti-oxidants.

TABLE II

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
12	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate	200	2	2
13	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; lauryl amine	200 500	0	0
14	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; stearyl amine	200 500	0	0
15	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol lauryl amine	200 500	0	0
16	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol stearyl amine	200 500	0	0
17	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol tallow amine	200 500	0	0
18	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; stearyl alcohol	200 500	2	3

TABLE II (continued)

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
19	Resin B			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	200	3	3
	glyceryl mono stearate	500		
20	Resin B			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	200	3	3
	sorbitan mono laurate	500		

Example 2

A series of tests was run as in Example 1 except as follows: Resin A based compositions were made via the first method disclosed previously herein. The films were extruded at 3 lbs/hr with a 380°F melt temperature using a one inch diameter Killion extruder equipped with a 1 1/4 inch spiral die (30 mil die gap). No nitrogen purge was employed except for run 21 which used a 1 SCFH rate into the extruder hopper. Table III below discloses the various formulations that were evaluated and the gel streaking/pinstriping rating of the extruded films. The films of runs 23 and 24 using formulations containing anti-gel compounds of this invention showed substantial improvement in gel streaking/pinstriping properties over those of control runs 21 and 22.

TABLE III

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
21	Resin A Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane	200	3	3
22	Resin A Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane	200	3	3
23	Resin A Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane; diethanol stearyl amine	200 500	0	0
24	Resin A Tetra-bis[methylene 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate]methane; dimethyl stearyl amine	200 500	0	1

Example 3

A series of tests was run as in Example 1 except as follows: Resin B based compositions were made via the second method disclosed previously herein. The films were extruded at 22-24 lbs/hr with a 410°F melt temperature using a 1 1/2 inch diameter 24 to 1 length to diameter Sterling extruder equipped with a 3 inch diameter spiral pin die (60 mil gap). No nitrogen purge was used on the extruder hopper. Table IV below discloses the various formulations that were evaluated and the gel streaking/pinstriping rating of the extruded films. The results of these runs, 25-29, show that for an ethylene-butene-1 copolymer, a ratio of anti-gel compound to anti-oxidant of 0.5 does not prevent gel streaking/pinstriping while an anti-gel/anti-oxidant compound ratio of 1 to 1 or greater does prevent gel streaking/pinstriping in the extruded films.

TABLE IV

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
25	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol cocoamine	 200 500	0	0
26	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol cocoamine	 200 100	3	3
27	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol tallow amine	 200 500	0	0
28	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol tallow amine	 100 250	0	0
29	Resin B Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate; diethanol tallow amine	 200 200	0	0

Example 4

Volatility of some anti-gel compounds was determined by thermal evolution analysis. This measurement, made with the DuPont model 916 Thermal Evolution Analyzer (TEA) determines the fraction of species present in a sample of less than approximately 500 molecular weight. A 5 mg sample is heated under nitrogen at 32°C/min up to 300°C. As the sample heats, evolved gases are swept by nitrogen to a flame ionization detector. Calibration with C_{20} standards permits translation of instrument output into volatile weight. Normalizing by sample weight and multiplying by 100 gives weight percent volatiles. The TEA volatiles for the fatty acid amines useful in this invention are all below about 5% by weight, as shown in Table V below:

TABLE V

Additive Volatility Using TEA

Additive	Weight Loss at 180°C (%)
diethanol lauryl amine	3.11%
diethanol mystearyl amine	2.30%
diethanol stearyl amine	0.06%

Example 5

A series of tests was run to demonstrate that the addition of the fatty acid amine to the extrudable film compositions does not adversely affect the physical properties of the extruded film to any substantial degree. Films made from Resin A based composition were evaluated in a discoloration and coefficient of friction test and films made from Resin B based composition were evaluated in a roll blocking test.

In the coefficient of friction test, the extrusion conditions were as follows: Resin A based compositions were extruded on a 2 1/2 inch diameter 24 to 1 length to diameter Egan extruder equipped with a 6 inch diameter Sano die having a 100 mil die gap. The extrusion rate was about 85 lbs/hr with a melt temperature of about 390°F. The extruded films were approximately 1.5 mils thick.

Table VI below sets forth the Resin A based compositions used for the coefficient of friction comparisons. The coefficient of friction is measured by ASTM D-1894-63. The data indicates that film made from a formulation containing a fatty acid amine did not have any significantly different coefficient of friction, as compared to a control formulation which did not contain the fatty acid amine, but was otherwise the same, in terms of composition, as the other formulation.

TABLE VI

Run	Formulation	Concentration (PPM)	Coefficient of Friction
30	Resin A		
	Octadecyl 3-(3'-5'-di-tert-butyl-4'-hydroxyphenyl) propionate;	300	30 min-0.11
	Tri-nonyl-phenyl phosphite ester;	200	24 hrs-0.11
	erucamide;	1000	
	superfloss	5300	
31	Resin A		
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl) propionate;	300	
	Tri-nonyl-phenyl phosphite ester;	200	30 min.-0.11
	erucamide;	1000	24 hrs-0.12
	superfloss (finely divided diatomaceous earth);	5300	
	diethanol stearyl amine	250	

In the roll blocking test, the Resin B based film compositions set forth in Table VII below were subjected to

induced blocking which was measured in grams (sample conditions for 24 hrs. at 60°C under a 0.14 psi load).

TABLE VII

Run	Formulation	Concentration (PPM)	Induced Blocking (gms)
32	Resin B		
	1,3,5-Tris(4-tert-butyl-3-hydroxy-2,6 dimethyl benzyl) -1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;	100	50
	Di-stearyl-pentaerythritol-diphosphite;	100	
	superfloss (finely divided diatomaceous earth);	5000	
	erucamide	800	
33	Resin B		
	1,3,5-Tris(4-tert-butyl-3-hydroxy-2,6 dimethyl benzyl) -1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;	100	
	Di-stearyl-pentaerythritol-diphosphite;	100	
	superfloss (finely divided diatomaceous earth);	5000	54
	erucamide;	800	
	diethanol tallow amine	500	

In the color rating test, films prepared from Resin A formulations as described hereinabove were aged 4 weeks at 60°C. The extruded film was made as described herein for Resin A compositions except a 60 mil die gap was employed with a 79 lb/hr extrusion rate. No discoloration was observed.

Example 6

A series of tests were run as described herein for example 1 for Resin A based composition made under the extrusion conditions of example 5 (60 mil die gap with 79 lb/hr extrusion rate). Gel streaking and pinstriping were evaluated for control compositions and Resin A based compositions containing fatty acid amines according to this invention. Table VIII sets forth the results which show a substantial improvement in gel

streaking/pinstriping properties for the films of the Resin A formulations of this invention (runs 35-38) over the control formulation (run 34).

TABLE VIII

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
34	Resin A			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate	125	2	3
35	Resin A			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	225	0	0
	Tri-nonyl-phenyl phosphite ester;	200		
	superfloss (anti-block);	5300		
	erucamide (slip agent);	1000		
	diethanol tallow amine	400		
36	Resin A			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	300	0	0
	Tri-nonyl-phenyl phosphite ester;	350		
	superfloss;	9300		
	erucamide;	1750		
	diethanol tallow amine	700		
37	Resin A			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	225	0	0
	Tri-nonyl-phenyl phosphite ester;	200		
	superfloss;	5300		
	erucamide;	1000		
	diethanol stearyl amine	400		

TABLE VIII (continued)

Run	Formulation	Concentration (PPM)	Gel Streaking Rating	Pinstriping Rating
38	Resin A			
	Octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate;	300	0	0
	Tri-nonyl-phenyl phosphite ester;	350		
	superfloss;	9300		
	erucamide;	1750		
	diethanol stearyl amine	700		

CLAIMS:

1. A process for extruding a film forming polyolefin resin based composition into film, which composition comprises a Ziegler-Natta catalyzed film grade polyolefin resin which contains a chloride residue in the range of between about 5 and about 500 ppm and anti-oxidant in the range of between about 20 and about 5000 ppm, which composition is susceptible to gel streaking and pinstriping during the formation of said film,

characterized by:

extruding said composition into said film in the presence of an acid acceptor, said acid acceptor being present in a concentration sufficient to neutralize said chloride residue in said composition, said concentration of acid acceptor being at least about 0.8 times the concentration of said anti-oxidant, said acid acceptor having a molecular weight ≥ 180 with $\leq 5\%$ by weight volatiles at 180°C as measured by thermal evolution analysis.

2. A process as defined in claim 1 wherein the acid acceptor comprises a fatty acid amine of the formula:

$$R-N\begin{matrix} R' \\ R'' \end{matrix}$$

wherein R is $C_{12}-C_{24}$ alkyl or alkylene;

R' is hydrogen, lower alkyl, alkanol, 1,3-propylene diamine or an ethoxy group of the formula: $(C-C-O)_xH$ wherein x is an integer between 2 and 5; and

R" is R or R'.

3. A process as defined in claim 2 wherein said

polyolefin is an ethylene polymer, said chloride residue concentration is between about 5 and about 50 ppm, said anti-oxidant concentration is between about 20 and about 500 ppm, and said fatty acid amine concentration is between about 25 and 1000 ppm.

4. A process as defined in claim 2 wherein said polyolefin resin is polypropylene or polybutene, said chloride residue concentration is between about 10 and about 500 ppm, said anti-oxidant concentration is between about 200 and about 5000 ppm, and said fatty acid amine concentration is between about 200 and about 10,000 ppm.

5. A process as defined in claim 2 wherein said fatty acid amine is present in an amount at least 5 times the amount of chloride residue present, preferably in a fatty acid amine to chloride residue ratio of greater than 10 to 1.

6. A process as defined in claim 3 wherein said ethylene polymer is low pressure, low density, ethylene-butene-1-copolymer.

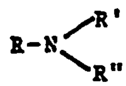
7. A process as defined in any of claims 2-6 wherein said fatty acid amine is lauryl amine, stearyl amine, or behenyl amine, or combinations thereof; diethanol lauryl amine, diethanol stearyl amine, diethanol behenyl amine, or combinations thereof; diethanol tallow-amine having between 14 and 18 carbon atoms or dimethyl soya amine having between 14 and 18 carbon atoms.

8. A process as defined in any of claims 1-7 wherein said polyolefin resin based composition is extruded under an extrusion temperature of at least 275°F to 650°F and a throughput time for said composition in the extruding equipment of about 0.2 to 10 minutes.

9. An extruded film essentially devoid of gel streaking and pinstriping producible according to the process of any of claims 1-8.

10. An extrudable film forming composition comprising a polyolefin resin containing a chloride residue, an anti-oxidant, and an acid acceptor, said chloride residue being present in a concentration between about 5 and about 500 ppm, said anti-oxidant present in a concentration between about 20 and about 5000 ppm, said acid acceptor being present in a concentration sufficient to neutralize said chloride residue, said concentration of acid acceptor being at least about 0.8 times the concentration of said anti-oxidant, said acid acceptor having a molecular weight $\geq$180 with $\leq$5% by weight volatiles at 180°C as measured by thermalevolution analysis.

11. A composition as defined in claim 10 wherein the acid acceptor comprises a fatty acid amine of the formula:



wherein R is C_{12}-C_{24} alkyl or alkylene;

R' is hydrogen, lower alkyl, alkanol, 1,3-propylene diamine or an ethoxy group of the formula: $(C-C-O)_xH$ wherein x is an integer between 2 and 5; and

R" is R or R'.

12. A composition as defined in claim 11 wherein said polyolefin is an ethylene polymer, said chloride residue concentration is between about 5 and about 50 ppm, said anti-oxidant concentration is between about 20 and about 500 ppm, and said fatty acid amine concentration is between about 25 and 1000 ppm.

13. A composition as defined in claim 11 wherein said polyolefin resin is polypropylene or polybutene, said chloride residue concentration is between about 10 and about 500 ppm, said anti-oxidant concentration is between about 200 and about 5000 ppm, and said fatty acid amine concentration is between about 200 and about 10,000 ppm.

14. A composition as defined in claim 11 wherein said fatty acid amine is present in an amount at least 5 times the amount of chloride residue present, preferably in a fatty acid amine to chloride resicue ratio of greater than 10 to 1.

15. A composition as defined in claim 12 wherein said ethylene polymer is low pressure, low density, ethylene-butene-1-copolymer.

16. A composition as defined in any of claims 11-15 wherein said fatty acid amine is lauryl amine, stearyl amine, or behenyl amine, or combinations thereof; diethanol lauryl amine, diethanol stearyl amine, diethanol behenyl amine, or combinations thereof; diethanol tallow amine having between 14 and 18 carbon atoms or dimethyl soya amine having between 14 and 18 carbon atoms.

17. A composition as defined in any of claims 10-16 further including a slip agent and an anti-block agent.

18. A process for slot casting, blown film extruding or injection or blow molding a Ziegler-Natta catalyzed film grade or molding grade polyolefin resin composition containing a chloride residue in the range of 5 to 500 ppm, characterized by slot casting or extruding said composition into a film or molding said composition under heat and pressure into a molded article

in the presence of an acid acceptor, said acid acceptor being present in a concentration sufficient to neutralize the chloride residue, said acid acceptor having a molecular weight ≥ 180 with $\leq 5\%$ by weight volatiles at 180°C as measured by thermal evolution analysis.

19. A process as defined in claim 18 wherein the acid acceptor comprises a fatty acid amine of the formula:

$$R{-}N\begin{matrix} \diagup R' \\ \diagdown R'' \end{matrix}$$

wherein R is C_{12}-C_{24} alkyl or alkylene;

R' is hydrogen, lower alkyl, alkanol, 1,3-propylene diamine or an ethoxy group of the formula: $(C{-}C{-}O)_xH$ wherein x is an integer between 2 and 5; and

R" is R or R'.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 81 11 0327

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D,X	US - A - 3 773 743 (O.C. AINSWORTH et al.) * Claims; column 2, lines 45-50; column 3, lines 25-28, lines 42-46 * --	1-18	C 08 J 5/18 C 08 F 6/24 C 08 L 23/02
A	FR - A - 1 410 555 (HOECHST) ----		

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 08 J
C 08 F
C 08 L

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
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E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons
&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	26-02-1982	VAN GOETHEM

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